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(56) Documents Cited
US 5458195 A US 4460730 A
US 4339273 A US 4297414 A
WPI Abstract Accession No.1989-280794 & JP1203249
WPI Abstract Accession No.1980-78126C & JP55121939

(58) Field of Search
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INT CL^7 C04B 16/04 16/06 16/12 20/10 24/30
Other: Online: WPI, EPODOC, PAJ

(54) Abstract Title

Cement comprising particulate phenol formaldehyde resin

(57) A cement composition comprises cement; water; and a particulate, phenol-formaldehyde material. The particulate, phenol-formaldehyde material can be a partially or essentially fully cross-linked resin. Preferably, the particles have a highly cross-linked shell and a partially cross-linked interior. The particles may be spherical, plate-like, ribbon-like or fibrous and their size may vary from less than 10 microns up to 300 microns. The solid components of the cement composition are combined to optimise the packing volume fraction. The use of a solid particulate material means that it can contribute to the physical properties of the cement as well as to the chemical behaviour. Highly cross linked resins are preferred where chemical and physical stability are required. Material having a molecular weight of greater than 10,000 is often preferred. The cement composition can be used to cement oil, gas or geothermal wells where high temperatures, pressures and physical stresses are encountered and the cement is exposed to high salinity brines and hydrocarbon formation fluids.

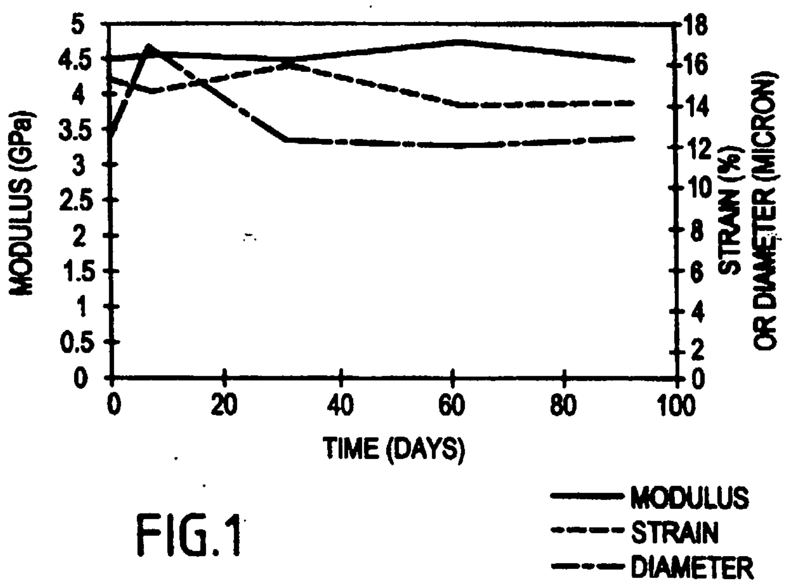

FIG.1

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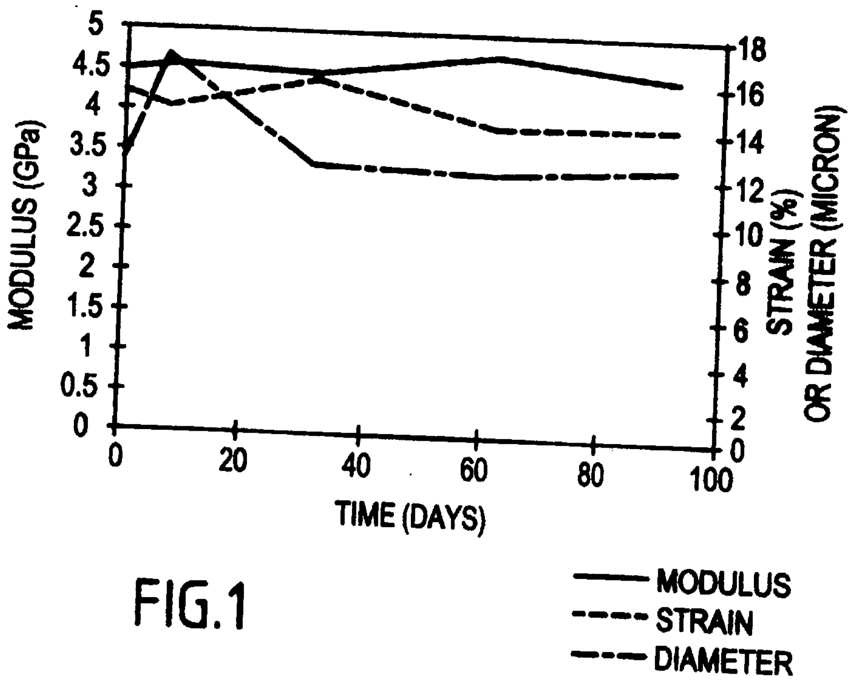
At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.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4
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1.5
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0
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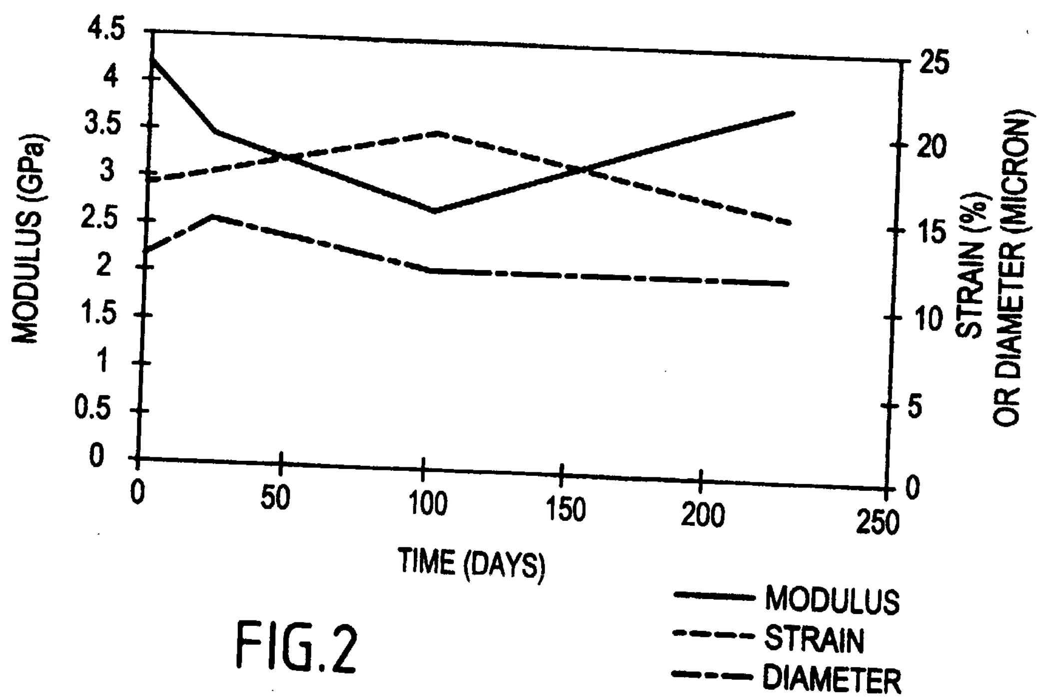
18
16
14
12
10
8
6
4
2
0
STRAIN (%)
OR DIAMETER (MICRON)
0
20
40
60
80
100
TIME (DAYS)
MODULUS
STRAIN
DIAMETER

FIG.1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4
3.5
3
2.5
2
1.5
1
0.5
0
MODULUS (GPa)
25
20
15
10
5
0
STRAIN (%)
OR DIAMETER (MICRON)
0
50
100
150
200
250
TIME (DAYS)
MODULUS
STRAIN
DIAMETER

FIG.2

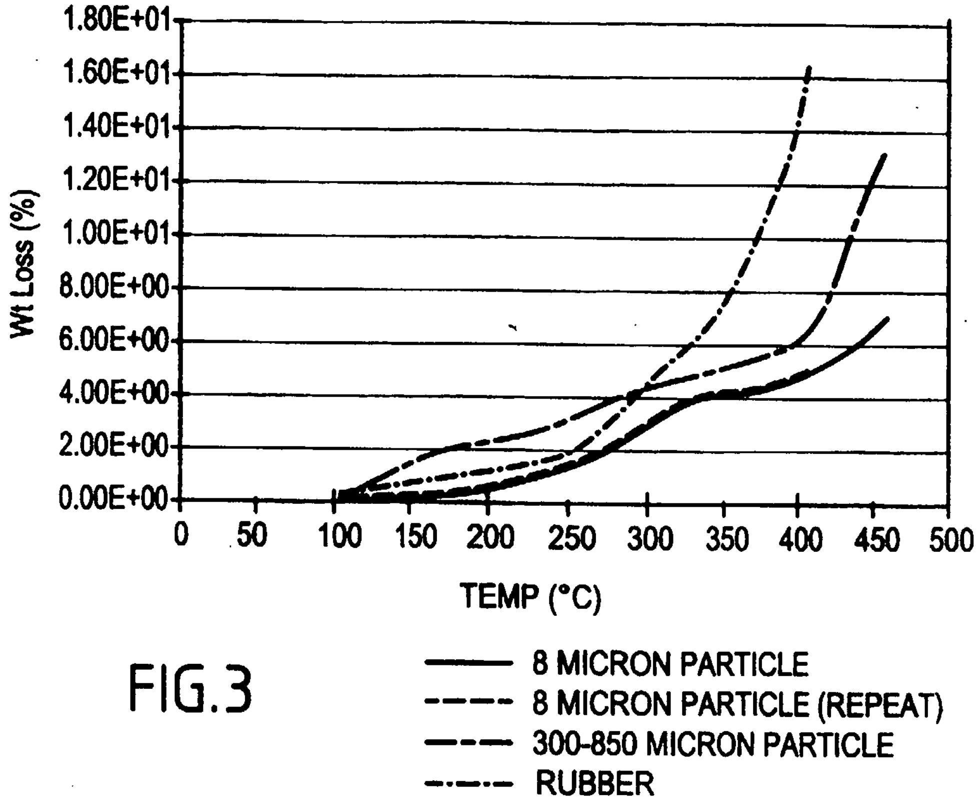

FIG.3

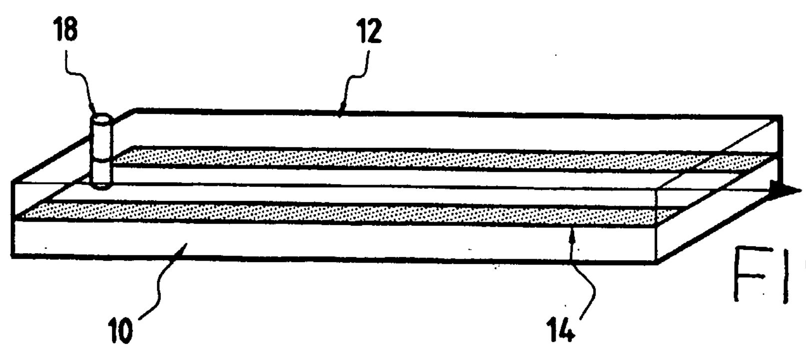

FIG 4a

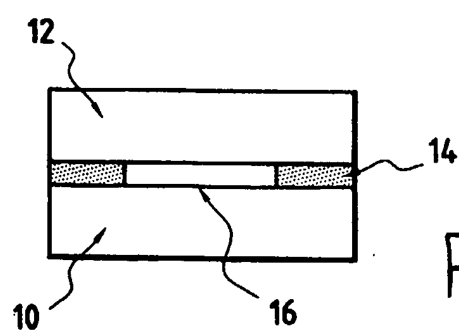

FIG 4b

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RESIN CEMENTS

The present invention relates to the use of phenol-formaldehyde resins in cements for use in oil wells or the like.

The use of resins, including phenol-formaldehyde resins, in cements has been previously proposed, particularly in an attempt to improve the physical performance of the set cement.

Phenol-formaldehyde resin chemistry is known to be highly resistant to chemical attack and stable at elevated temperatures. A well-known example of a phenol-formaldehyde resin is Bakelite. Other examples illustrating the properties of such resins can be found in US 5,5782,300 and SPE 39960. The chemistry of phenol-formaldehyde resins includes that of resole resins, novolac resins, phenolic resins and similar resins. Such chemistry also includes phenol-formaldehyde-like resins such as acetylated novoloid fibres.

Certain applications of phenol-formaldehyde resins have been proposed in the field of cements. Examples include US 6,065,539 and US 5,569,324 in which liquid phenol-formaldehyde resins, prior to significant cross-linking, are included in cement slurries. Liquid, partially cross-linked resins have also been included in high solids concentration cements to give physical and chemical benefits to the resulting cement, as is described in Advanced Cement Based Materials, Volume 6, #2, August 1997 pp 45 – 52. However, such cements are not pumpable in the manner of oilfield cement slurries.

The use of solid resin materials in oilfield cement slurries is known, in particular for providing toughness to the resulting cement. Flexible materials, such as polyproylene and rubber have been included in oilfield cement slurries for use in cementing zones of wells subjected to extreme physical stresses such as perforation zones and junctions of multilateral wells. Examples of such uses are found in WO 00/37387 and WO 00/20350.

Novoloid fibres (20mm x 20 μm) have been included in oilfield cement slurries pumped to address lost circulation problems.

It is an object of the present invention to provide a cement slurry that is suitable for use in oilfield applications and which benefits from the properties of solid phenol-formaldehyde materials.

In accordance with the present invention, there is provided a cement composition comprising:

- cement;
- water; and
- a particulate, phenol-formaldehyde material.

Other additives commonly used in cements can be included in the composition according to requirements.

The particulate, phenol-formaldehyde material can be a partially or essentially fully cross-linked resin. The use of a solid particulate material means that it can contribute to the physical properties of the cement as well as to the chemical behaviour. Highly cross linked resins are preferred where chemical and physical stability are required. Material having a molecular weight of greater than 10,000 is often preferred. Examples of fully cross-linked phenol-formaldehyde resins are BellPearl R800 from Kanebo Ltd., Maririn HF from GunEi Chemical, and Novoloid fibres from Nippon Kynol. An example of a partially cross-linked phenol-formaldehyde resin particulate material is BellPearl S899 from Kanebo Ltd.

Particulate material having an highly cross-linked shell and an partially cross-linked interior can be used to provide delayed release of the reactive interior component into the cement composition, where it may react with other cement components.

The size and shape of the particulate material can be chosen according to requirements. In particular, when the cement composition is one having an engineered particle size distribution, the resin can comprise part or all of one or more of the

particle size fractions. For example, resin particles can be obtained in sizes corresponding to a coarse particle size range ($\simeq$ 300 micron), medium particle size range ($\simeq$ 30 micron) or fine particle size range (< 10 micron). The solid components of the cement composition forming these fractions can be combined to optimise the packing volume fraction (PVF = portion of the volume occupied by particulate material that is occupied by solid material). This approach is describe in more detail in EP 0 621 247 B, which describes a cement composition formed from particles having controlled particle size ranges or granulometries. By optimising the packing volume fraction of the particulate materials, cement slurries can be designed that have improved properties while remaining pumpable in normal field conditions.

Also, the particle size can be chosen to meet other requirements. For example, for squeeze cementing operations, the particulate components of the cement slurry should be as small as possible. In this case a particle size of less than 10 microns is preferred.

The particulate phenol-formaldehyde material preferably has a spherical particle shape (size in all dimensions is approximately the same). However, plate-like particles (size in 1^{st} and 2^{nd} dimension >> size in 3^{rd} dimension), ribbon structures (size in 1^{st} dimension > size in second dimension > size in 3^{rd} dimension), or fibre structures (size in 1^{st} dimension >> size in 2^{nd} and 3^{rd} dimensions) are also possible.

Compositions of the present invention are particularly useful for cementing oil wells or the like when aggressive conditions are encountered, such as high temperatures or pressures, high salinity brines and hydrocarbon formation fluids, tectonic stresses, perforations or other physical stresses and the like. Such cement compositions also find uses in cementing pipes in geothermal wells which have to convey very high temperature water.

The present invention will now be described by way of examples and with reference to the following drawings, in which:

Figure 1 shows the effect of ageing in diesel oil on phenol-formaldehyde resin fibres;
Figure 2 shows the effect of ageing in steam on phenol-formaldehyde resin fibres;
Figure 3 shows the effect of heating on phenol-formaldehyde particles; and

Figures 4a and 4b show an experimental set-up for testing compositions according to the invention.

Example 1

In this example, the stability of phenol-formaldehyde resins in hydrocarbons at high temperature is demonstrated.

Phenol-formaldehyde fibres (Novoloid fibres from Nippon Kynol, ~15 microns diameter, length~30 cm) are placed in diesel oil in a pressure vessel and heated to 450°F (232°C) and maintained at this temperature for three months. Periodically, the vessel is cooled and several fibres removed and their mechanical properties tested. Figure 1 plots the development of Modulus, Strain and Fibre Diameter against time for this test. Each result is an average of 10 measurements on ten separate fibres. The results show that the fibres are essentially unaffected by exposure to the diesel oil, indicative of the stability of such materials in downhole environments.

Example 2

In this example, the stability of phenol-formaldehyde resins in water at high temperature is demonstrated.

Phenol-formaldehyde fibres (Novoloid fibres from Nippon Kynol, ~15 microns diameter, length~30 cm) are placed in water in a pressure vessel and heated to 350°F (177°C) and maintained at this temperature for three months. Periodically, the vessel is cooled and the fibre removed and their mechanical properties tested. Figure 2 plots the development of Modulus, Strain and Fibre Diameter against time for this test. The results show that the fibres are essentially unaffected by exposure to the water, indicative of the stability of such materials in downhole environments.

Example 3

In this example, the stability of phenol-formaldehyde resins at high temperature is demonstrated.

Samples of highly cross-linked phenol-formaldehyde resins (BellPearl R800 and Maririn HF) having particle sizes of 8 microns and 300 – 850 microns respectively

and a ground rubber product commonly used in oilfield cements (ground rubber particles having a particle size in the range of 250 – 425 microns) are subjected to thermogravimetric analysis with a heating rate of 2.5°C/min in a nitrogen atmosphere, rapid loss of weight indicating thermal degradation of the material. The results of the analysis are shown in Figure 3. The resin particles are much more stable than the rubber. Rapid weight loss for the resin occurs above 400°C compared to the 250°C for the rubber. Weight loss of the resin particles below 400°C is due to the increase in cross-linking level liberating water and sublimating trace amounts of salt remaining from the fabrication process. The larger particles are more susceptible to this as they are initially less cross-linked compared to the smaller particles.

Example 4

In this example, the ability of phenol-formaldehyde resins to provide flexibility to cement slurries is demonstrated.

The addition of flexible materials to oilfield cement slurries is well known, see for example WO 00/37387, WO/20350 and SPE 38598. While the materials proposed, ground rubber or polypropylene are effective in many cases, sustained high temperatures can cause problems. For example, polypropylene particles melt at 166°C and rubber degrades at 250°C (see above) and is attacked by solvents and hydrocarbons at lower temperatures.

Trimodal slurries A and B are prepared as summarised in Table 1 below. The slurries are identical in terms of volumes of solid constituents but Slurry A includes polypropylene particles (~200-800 microns diameter) and Slurry B includes phenol-formaldehyde resin particles(Maririn HF 300-850 microns diameter).

TABLE 1	Slurry A (Polypropylene)	Slurry B (Phenol-Formaldehyde)
Cement (Class G)	333.68g/600ml	333.68g/600ml
Micro-Silica	118.06g/600ml	118.06g/600ml
Polypropylene particles	163.35g/600ml	-
Phenol-Formaldehyde	-	230.51g/600ml
Antifoam	1.53g/600ml	1.70g/600ml
Fluid Loss Additive	19.39g/600ml	21.47g/600ml
Dispersant	2.23g/600ml	2.47g/600ml

Porosity	45%	45%
Density	12.33 lb/gal	13.25 lb/gal

In both cases, equal volumes of flexible particles are added, density differences leading to the difference in mass and slurry density. The concentrations of antifoam, dispersant and fluid loss additive are added at a constant ratio per mass of solids.

Samples of each slurry are cured at 300°F and 3000psi for 3 days which is sufficient time for the maximum compressive strength to be obtained. After curing, cubes of set cement are crushed in a hydraulic press and the Young's modulus and maximum compressive strength measured. The results are shown in Table 2 below:

TABLE 2	Slurry A	Slurry B
Young's modulus	2059 $\pm$ 647 MPa	1173 $\pm$ 850 MPa
Compressive Strength	22.3 $\pm$ 0.8 MPa	16.3 $\pm$ 3.2 MPa
Compressive Strength/Modulus	0.011	0.014

The data show that compositions according to the invention can provide flexibility and strength at temperature.

Example 5

In this example, the ability of compositions including phenol-formaldehyde resin particles to pass through small gaps is demonstrated.

Fine (<20 micron) phenol-formaldehyde particles can be added to an optimised microcement composition without impacting the ability of the slurry to pass though small gaps (~ 120 microns width). In this example, a higly cross-linked phenol-formaldehyde resin (BellPearl R800 from Kanebo Ltd., nominal particle size 8 microns) is included in a cement slurry. The particles are approximately spherical and so allow relatively easy mixing in slurries. Three sample slurries are prepared and summarised in Table 3 below. Slurry A is a basic microcement formulation, while Slurries B and C have a portion of the microcement replaced by quantities of resin particles. The dispersant and retarder are kept at a constant ratio with the cement whilst the fluid loss additive and antifoam agent are kept at a constant ratio with the total liquid volume of the slurry.

TABLE 3	Slurry A	Slurry B	Slurry C
Microcement	601.8g/600ml	361.08g/600ml	424.8g/600ml
BellPearl R800	-	103.63g/600ml	121.92g/600ml
Retarder	1.02g/600ml	0.61g/600ml	0.72g/600ml
Dispersant	45.27g/600ml	27.17g/600ml	31.97g/600ml
Fluid Loss Additive	141.07g/600ml	141.07g/600ml	128.25g/600ml
Antifoam	18.28g/600ml	18.28g/600ml	16.61g/600ml
Water	202.73g/600ml	217.75g/600ml	191.88g/600ml
Porosity	66%	66%	60%
Density	14.0 ppg	12.09 ppg	12.74 ppg

The properties of the slurries are tested in the setup shown in Figure 4. This comprises a permeable base block including a filter paper 10 and a Perspex plate 12 mounted above the base block 10 on spacers 14 mounted along parallel sides to leave a channel 16 of 120 micron thickness, 30mm width and 24.5 cm length therebetween. One end of the Perspex plate 12 is provided with an injection port 18 and the channel is closed at that end such that fluids injected into the channel have to pass along its length in order to flow out of the test setup.

Each cement slurry is injected into the system from a syringe at a fixed flow rate and a maximum injection pressure. Fluid loss occurs through the base block and filter paper 10. If the slurry contains particles that are too large, or if the fluid loss is not properly controlled, solids will build up in the channel and the maximum injection pressure will be reached and the test stopped. Non-optimised class G slurries cannot flow through this setup. All three slurries A – C pass this test demonstrating that the phenol-formaldehyde particles do not interfere with the capability of the slurry to penetrate small spaces.

Example 6

This example demonstrates the resistance to aging of compositions according to the invention.

The slurries are prepared. Slurry A is a basic Class G cement slurry with cement and an antifoam agent. Slurry B is a conventional, flexible slurry containing rubber particles, a dispersing agent (polynaphthalene sulphonate), a retarder (lignosulphonate), and an antifoam agent (silicone). Slurry C is a phenol-formaldehyde resin-containing composition according to the invention. As well as the cement and resin particles (highly cross-linked resin beads 300 – 800 microns in diameter), Slurry C also contains a dispersing agent and a fluid loss additive and micro-silica to prevent strength retrogression. The compositions are summarised in Table 4 below ("bwoc" = by weight of cement; "gps" = gallons per sack):

TABLE 4	Slurry A	Slurry B	Slurry C
Micro-Silica	-	-	35.5% bwoc
Phenol-Formaldehyde Resin	-	-	69.3% bwoc
Rubber	-	30.6% bwoc	-
Dispersant	-	0.037 gps	0.067 gps
Retarder	-	0.025 gps	-
Antifoam	0.03 gps	-	-
Fluid Loss Additive	-	-	0.0674 gps
Porosity	58%	45%	45%
Density	1.89 g/cm^3	1.69 g/cm^3	1.59 g/cm^3

Slurries A and B are cured in 5 cm cubic moulds at 77°C and 3000 psi for several days to set. Samples of Slurry C are cured in similar moulds under different conditions:

(i) 77°C atmospheric 2 days

(ii) 150°C 3000 psi 3 days

(iii) 250°C 3000 psi 3 days

(iv) 300°C 3000 psi 3 days

Compressive strength and Young's modulus are measured as before and summarised in Table 5 below:

TABLE 5	Conditions	Young's Modulus	Compressive Strength
Slurry A		6275 MPa	36.6 MPa
Slurry B		1615 MPa	10.1 MPa
Slurry C	(i)	1663 MPa	9.0 MPa

	(ii)	684 MPa	16.4 MPa
	(iii)	1376 MPa	19.4 MPa
	(iv)	1714 MPa	5.5 MPa

Under similar curing conditions, the resin system gives similar properties to a conventional rubber-based, flexible system with a Young's modulus that is about ¼ of that of a comparable neat cement system. At elevated temperatures, the resin system retains good properties with low Young's modulus and a compressive strength of > 5MPa. Thus the flexibility is retained even under conditions in which conventional systems are unstable.

CLAIMS

1 In accordance with the present invention, there is provided a cement composition comprising:

- cement;
- water; and
- a particulate, phenol-formaldehyde material.

2 A composition as claimed in claim 1, wherein the particulate, phenol-formaldehyde material is a partially or essentially fully cross-linked resin.

3 A composition as claimed in claim 2, wherein the particulate, phenol-formaldehyde material is a highly cross-linked resins having a molecular weight of greater than 10,000.

4 A composition as claimed in claim 1 or 2 wherein the particulate, phenol-formaldehyde material has a highly cross-linked shell and an partially cross-linked interior.

5 A composition as claimed in any preceding claim, wherein the particulate, phenol-formaldehyde material is provided with a discrete particle size distribution comprising one or more of a coarse particle size range ($\simeq$ 300 micron), medium particle size range ($\simeq$ 30 micron) or fine particle size range (< 10 micron)

6 A composition as claimed in any preceding claim, wherein the solid components are combined to optimise the packing volume fraction.

7 A composition as claimed in any preceding claim, wherein the particulate, phenol-formaldehyde material has a particle size of less than 10 microns.

8 A composition as claimed in any preceding claim, wherein the shape of the particulate phenol-formaldehyde is spherical particle, plate-like, ribbon-like, or fibrous.

9 A method of cementing oil, gas or geothermal wells, comprising pumping a cement composition as claimed in any preceding claim into the well.

10 A method as claimed in claim 9 wherein the composition is pumped into a portion of the well in which aggressive conditions are encountered.

11 A method as claimed in claim 10, comprising pumping the composition into a region of high temperatures or pressures, high salinity brines and hydrocarbon formation fluids, tectonic stresses, perforations or other physical stresses.

12 A method as claimed in claim 9, 10 or 11, wherein the cement composition is pumped around the outside of a pipe or casing.

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Applicati n N :	GB 0203505.3	**Examiner:**	Kathryn Orme
Claims searched:	1-12	**Date of search:**	30 July 2002

12

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.T): C1H (HAS, HCH)

Int Cl (Ed.7): C04B 16/04, 16/06, 16/12, 20/10, 24/30

Other: Online: WPI, EPODOC, PAJ

Documents considered to be relevant:

Category	Identity of document and relevant passage		Relevant to claims
X	US 5458195	(TOTTEN ET AL) see especially column 4 lines 10-58 and column 5 lines 1-37	1 & 9-12
X	US 4460730	(KOYAMA ET AL) see especially column 3, column 5 lines 20-24 and 55-60, column 8 lines 23-31, column 11 lines 14-20, column 13 lines 58-65 and column 14 lines 52-54.	1,2,5,7 & 8
X	US 4339273	(MEIER ET AL) see especially column 6 lines 45-55	1 & 8
X	US 4297414	(MATSUMOTO) see especially column 1 lines 7-10, column 2 lines 4-6, 30-31 and 58-62	1,2 & 8
X	WPI Abstract Accession No. 1989-280794 & JP 1203249 (Ohbayashi Corp) 16/08/1989 (see abstract)		1
X	WPI Abstract Accession No. 1980-78126C & JP 55121939 (Showa Denko KK) 19/09/1980 (see abstract)		1 & 8

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
		E	Patent document published on or after, but with priority date earlier than, the filing date of this application.
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